



## Short communication

Proton exchange membrane fuel cell made of magnetron sputtered Pt–CeO<sub>x</sub> and Pt–Co thin film catalysts

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## H I G H L I G H T S

- Single PEMFC was made exclusively of thin film catalysts.
- The Pt–CeO<sub>x</sub> thin film (30 nm) anode catalyst was deposited by RF magnetron sputtering on the nanostructured GDL.
- The Pt<sub>60</sub>Co<sub>40</sub> thin film (50 nm) cathode catalyst was deposited by DC magnetron sputtering on the nanostructured GDL.
- Pt mass activity was 2.4 kW g<sup>−1</sup>(Pt).
- Pt loading was 50 μg of Pt per 1 cm<sup>2</sup> of MEA.

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## A B S T R A C T

Preparation of catalysts for proton exchange membrane fuel cells (PEMFCs) is of growing interest during last years. The magnetron sputtering technique is a promising method of catalyst preparation because it permits to synthesize catalysts in a fast and relatively less expensive way, however control of specific surface and durability of such catalysts still remains the main concern. We tested a single cell PEMFC catalyzed by using exclusively thin film approach by combining state-of-the art Pt-doped cerium oxide anode and a new Pt–Co alloy cathode. We have shown that beside very high mass activity of the catalysts relative to the membrane electrode assembly the catalyst nanoporous structure exhibits excellent stability and no sintering which generally represents the main drawback of ultrathin film.

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## 1. Introduction

Preparation of catalysts using thin film (TF) techniques is not outspread in heterogeneous catalysis yet because TF technologies are generally considered as incompatible with the preparation of sufficiently large surface areas. Moreover catalytic loading of large-sized reactors is not possible. These arguments, however, are not valid for the proton exchange membrane fuel cell (PEMFC) application. The TF coating technology for supported catalysts can be scaled, with the size of the deposition facility being the only limitation. Most importantly, however, high-surface-area nanoporous catalyst films can indeed be prepared by suitable deposition techniques [1–7].

Platinum is the most versatile element in catalysis, but its high price limits large-scale applications, for example in fuel cell technology. To maximize the noble metal efficiency, Pt should be atomically dispersed and located at the very surface layer of the material. Such atomically dispersed Pt surface species can be prepared with exceptionally high stability. We identify a specific structural element, a ceria “nanopocket”, which binds Pt<sup>2+</sup> so strongly that it withstands sintering and bulk diffusion [8]. These new materials may help to reduce the demand for noble-metals in catalytic applications. One example is the deposition of Pt-doped cerium oxide TFs on nanostructured carbon surfaces [5–9] which can be used for preparation of stable PEMFC anodes with extremely low Pt loading.

One of the main obstacles to the commercialization of fuel cells today is significant kinetic limitations for the oxygen reduction reaction (ORR) together with Pt cost. Therefore, it is essential for

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these limitations on Pt to be overcome or, at least, significantly reduced. In last 5 years many studies have shown that e.g. Pt–Co alloy catalysts could improve the catalytic activity and stability relative to pure Pt, e.g. Refs. [10–13], and enhancement in electrocatalytic activity has been interpreted in different ways. However, practically all studies report on Pt–Co alloy nanoparticles prepared by wet techniques. In this FC made by using thin film approach we used Pt–Co sputtered alloy by co-sputtering Pt and Co.

In order to make fuel cell technology economic and competitive the FC cost should continue to reduce, e.g. by increasing PEMFC power output per gram of Pt. U.S. Department of Energy target for Pt mass activity was established at 6.0 kW per g in 2014 [14]. In this work we are presenting our first study of the PEM single FC made exclusively with thin film catalysts. Our results show promising future of this technology and it seems reasonable to expect that further improvement of deposition parameters, catalyst film stoichiometry and decrease of the cathode TF thickness could approach the above mentioned U.S. Department of Energy target.

## 2. Experiment

The nonreactive magnetron sputtering was used to prepare Pt–CeO<sub>x</sub> thin films and Pt–Co thin film catalysts. The Pt–CeO<sub>x</sub> anode catalyst layer was prepared by means of two magnetrons working simultaneously. RF sputtering of ceria was performed by using a 51 mm diameter CeO<sub>2</sub> target at distance of 90 mm from substrates. Pt was added by using the second DC operated magnetron at distance of 200 mm from substrates and tilted by 45° relative to the CeO<sub>2</sub> target. RF power (13.56 MHz) applied to the CeO<sub>2</sub> target was 50 W while power applied to the Pt target was 10 W. The sputtering was carried out in Ar atmosphere with total pressure of  $4 \cdot 10^{-1}$  Pa. The sputtering conditions gave a growth rate of the Pt-doped cerium oxide films of 1 nm min<sup>-1</sup>. The cathode Pt–Co catalyst was prepared by using the same procedure using a 51 mm diameter Co target instead of the CeO<sub>2</sub> one. Power of 20 W was applied to the both Co and Pt targets; the total pressure of argon working atmosphere was kept at  $6 \cdot 10^{-1}$  Pa. The sputtering conditions gave a growth rate of the Pt–Co films of 3.3 nm min<sup>-1</sup>. The catalyst film thicknesses were determined by Atomic Force Microscopy (AFM) from the reference films deposited on the silicon substrate simultaneously.

X-ray photoelectron spectroscopy (XPS) was performed in an ultrahigh vacuum (UHV) experimental chamber operating at base pressures  $<5 \cdot 10^{-10}$  mbar and equipped with a SPECS Phoibos MDC 9 electron energy analyzer and a dual Mg/Al X-ray source.

The FC tests were performed at 70 °C by using a device with pneumatically compressed graphite cell (Greenlight TP-5 Research Cell) using 800 kPa piston pressure. We used MEA with an active area of 4.6 cm<sup>2</sup> formed from the 0.05 mm thick Nafion membranes (DuPont Inc., Nafion NR-212, perfluorosulfonic acid-PTFE

copolymer), which was sandwiched by the catalyzed anode and cathode without hot-pressing. The commercial nGDL supports (SGL TECHNOLOGIES GmbH, Sigratec GDL 25 BC) coated by 30 nm thick Pt–CeO<sub>x</sub> layer (Pt contents 2 µg Pt cm<sup>-1</sup> of MEA) and by 50 nm thick Pt–Co layer (50 wt% Pt, Pt contents 48 µg Pt cm<sup>-1</sup> of MEA) have been used as a FC anode and cathode, respectively. The flow rates of hydrated H<sub>2</sub> and O<sub>2</sub> were controlled at 40 ml min<sup>-1</sup> and 30 ml min<sup>-1</sup>, respectively, Pt loadings were calculated from the film thickness and Pt concentration determined by XPS.

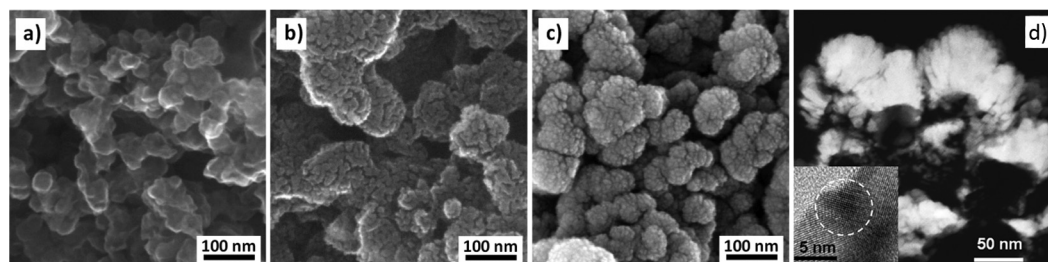
The in-situ Cyclic Voltammetry (CV) measurements (in 2 electrode set-up) were performed with the flow rates of 30 sccm of moistened hydrogen and 30 sccm of moistened nitrogen on the side of reference-counter electrode and on the side of working electrode respectively. The pressure of gases was ambient pressure, temperature was kept at 70°, the scan rate was 100 mVs<sup>-1</sup>.

Hydrogen treatment of the anode catalyst simulating the FC working condition was performed using temperature and digital flow meter controlled flow reactor. Morphology and structure of Pt–CeO<sub>x</sub>/nGDL were observed by means of Scanning Electron Microscopy (SEM) Tescan MIRA III microscope operating at 30 keV electron beam energy and by Transmission Electron Microscopy (TEM) using the 200 kV JEOL 2100F microscope with a Scherzer resolution of 0.19 nm. The samples for TEM observation have been prepared by using Focus Ion Beam (FIB) (Tescan LYRA FIB-SEM) technique of thin lamellas cut from the catalyst films.

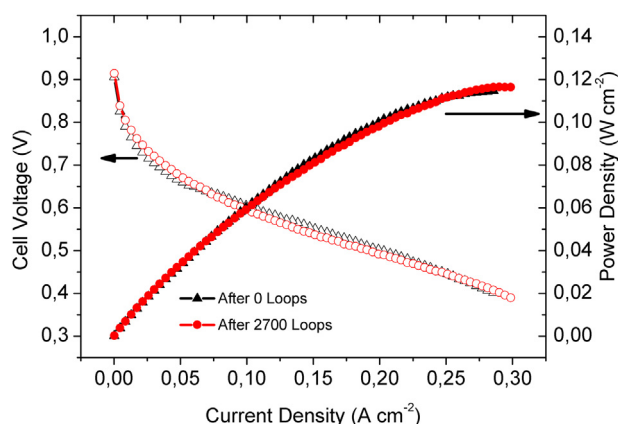
## 3. Results and discussion

Both anode and cathode thin film catalysts were deposited by magnetron sputtering on the nanostructured GDL (nGDL) which was composed of carbon nanoparticles of average size 50 nm as it can be seen in the SEM image in Fig. 1(a). Figure shows that the nGDL is formed by highly porous carbon particle conglomerates ensuring large specific surface of the substrate and a good diffusion of the gas feed to the catalyst film. Fig. 1(b) shows details of the nGDL surface covered by the anode Pt–CeO<sub>x</sub> catalyst layer. The catalyst film coating carbon particle surface reveals itself a nanoporous structure which is typical for the cerium oxide catalyst film sputtered on the carbon substrates, e.g. CNTs [5,7,15]. Fig. 1(c) shows structure of the Pt–Co catalyst. It is seen that coating exhibits cauliflower-like structure with average size of grains of 15 nm.

Scanning TEM and HRTEM (figure inset) micrographs in Fig. 1(d) show cross-section image of the Pt–Co catalyst thin lamella cut from the catalyst film deposited on the nGDL. STEM micrograph shows clearly carbon nanoparticles of the GDL (black) coated by columnar nanostructure of the catalyst film (bright) HRTEM figure inset shows presence of crystalline nanoparticles with average size 5 nm. Typical lattice structure, indicated by white circle, can be associated with (100) planes of the FCC lattice. Inter-planar distance 0.38 nm shows that this structure corresponds to Pt and/or



**Fig. 1.** SEM images of the nGDL (a), the sputtered Pt–CeO<sub>x</sub> 30 nm thick layer on the nGDL (b) and the Pt<sub>60</sub>Co<sub>40</sub> 50 nm thick layer on the nGDL (c). STEM and HRTEM (inset image) micrographs (d) show structure of the Pt–Co film deposited on carbon support particles.



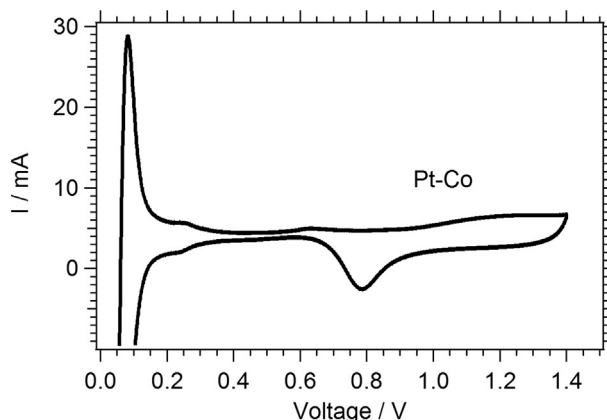
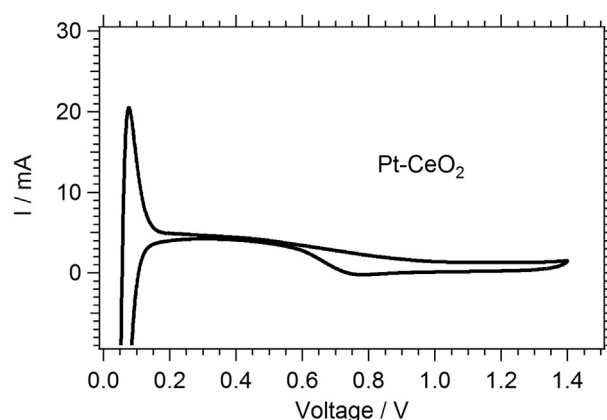
**Fig. 2.** I–V polarization curve and power density plot of fresh MEA (black triangles) and after durability test (red circles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Pt<sub>3</sub>Co particles [16]. HRTEM analysis of Pt–CeO<sub>2</sub> was already shown in our previous work [8], as it was mentioned in the introduction part.

The FC test was performed using the PEMFC described in section 2. The polarization I–V curve is shown in Fig. 2 together with the power density (PD) characteristics giving Pt mass activity in W cm<sup>-2</sup> of MEA. Pt content in both catalysts was determined by quantitative XPS: 2 μg cm<sup>-2</sup> of Pt at the anode and 48 μg cm<sup>-2</sup> of Pt at the cathode, respectively. With obtained maximum power density PD = 0.125 W cm<sup>-2</sup> and the value of Pt loading we determined FC specific power (Pt mass activity) SP = 2.5 kW g<sup>-1</sup>(Pt), see Table 1. We note that replacement of the Pt–Co catalysts by pure sputtered Pt layer 50 nm thick gave similar fuel cell power density as Pt–Co but lower mass activity because of higher total Pt loading of 100 μg cm<sup>-2</sup>. This observation supported generally accepted idea of a formation of Pt rich skin on the catalyst surface.

The in-situ characterization of membrane catalysts films by CV performed directly in the fuel cell was used to measure an electrochemical active surface area (ECSA) of the catalyst at the end of the FC test. The CV experiment was performed using the standard two-electrode set-up: The counter electrode and the reference electrode together were connected to side fed by a moistened hydrogen flow and the working electrode was connected to the side of interest keeping under a moistened nitrogen flow.

The CV from Pt–CeO<sub>x</sub> anode is shown in Fig. 3(a) and the CV from Pt–Co cathode is shown in Fig. 3(b). In figures it is clearly seen that both materials are catalytically active. Both CVs clearly show Pt–O reduction peaks and high hydrogen adsorption/desorption peaks in region 0–0.4 V. Similarly to FC tests, these results confirm high catalytic activity of both materials. In case of both CVs, relatively high hydrogen evolution appeared. The reason was that the non-standard platinum–hydrogen electrode consisted of platinum based catalyst (Pt–CeO<sub>2</sub> or Pt–Co) and fed by flow of hydrogen was used as a reference. The exact potential against to reversible hydrogen electrode (RHE) was difficult to determine and the data



**Fig. 3.** In-situ cyclic voltammetries of Pt–Co cathode and Pt–CeO<sub>x</sub> anode.

has shown as obtained. The shift to the positive current in both CVs was due to crossover of hydrogen [17] which was 0.6 mA cm<sup>-2</sup>. The CV profile obtained for Pt–Co in Fig. 3(b) is similar to that of the active disordered Pt<sub>3</sub>Co cubic phase CV [10] confirming suggestion of a Pt rich skin formation.

The calculated active area of both Pt–CeO<sub>x</sub> and Pt–Co catalysts was determined as 460 and 20 m<sup>2</sup> g<sup>-1</sup>(Pt), respectively (see Table 1).

As we have shown previously, sputtered Pt-doped cerium oxide contains Pt in Pt<sup>2.4+</sup> state [6–9]. In the PEMFC a mixture of hydrogen and water vapor is used as a feed stream due to necessity to keep the proton exchange membrane wet. Consequently during the FC working conditions the anode catalyst is reduced and for very low loading (case of this work) Pt<sup>4+</sup> is transformed to Pt<sup>2+</sup>. Fig. 4 shows Pt 4f spectrum obtained after annealing in wet H<sub>2</sub> at 65 °C in the flow reactor simulating anode conditions of the PEMFC operation. The spectrum of hydrogen annealed Pt–CeO<sub>x</sub> shown in Fig. 4 confirms that there is only one 4f<sub>7/2</sub>–4f<sub>5/2</sub> doublet at binding energy (BE) 72.5–75.8 eV corresponding to Pt<sup>2+</sup> [5]. Recently we have shown that formation of Pt<sup>2+</sup> ionic platinum results from its atomic dispersion [8] which explains very high ECSA of Pt, see Table 1.

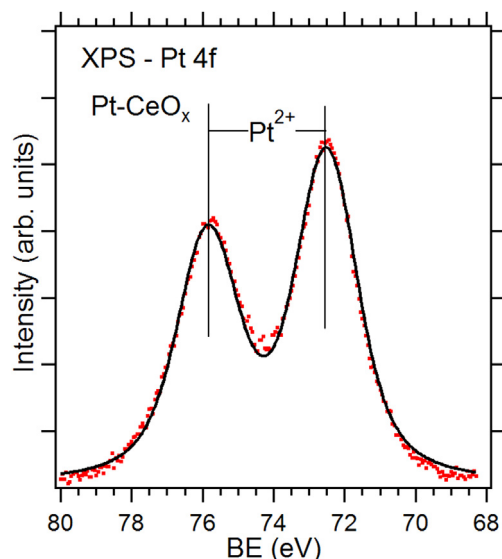
XPS analysis of the Pt–Co alloy thin film used as a cathode is shown in Fig. 5(a–c). The Pt 4f spectrum presented in Fig. 5(a) shows that Pt has metallic character which is seen from doublet at BEs 71.2–74.5 eV and asymmetric shape of the Pt 4f peaks characteristic for metallic Pt.

The Co 2p<sub>3/2</sub> region of the XPS spectrum in Fig. 5(b) can be fit by four peaks, two peaks at 780.9 eV and 786 eV indicating Co<sup>2+</sup> as predominant species, one peak at 779.9 eV corresponding to Co<sup>3+</sup> and a peak of metallic Co at 778.6 eV [18]. The highest peak at

**Table 1**

The power density, specific power, platinum loading and the electrochemical active area for Pt–CeO<sub>x</sub> and Pt–Co catalyst.

Catalyst	PD mW cm <sup>-2</sup>	SP kW g <sup>-1</sup> Pt	Pt loading μg cm <sup>-2</sup>	ECSA m <sup>2</sup> g <sup>-1</sup>
Pt–CeO <sub>x</sub> + Pt <sub>50</sub> Co <sub>50</sub>	125	2.5	50	460/20

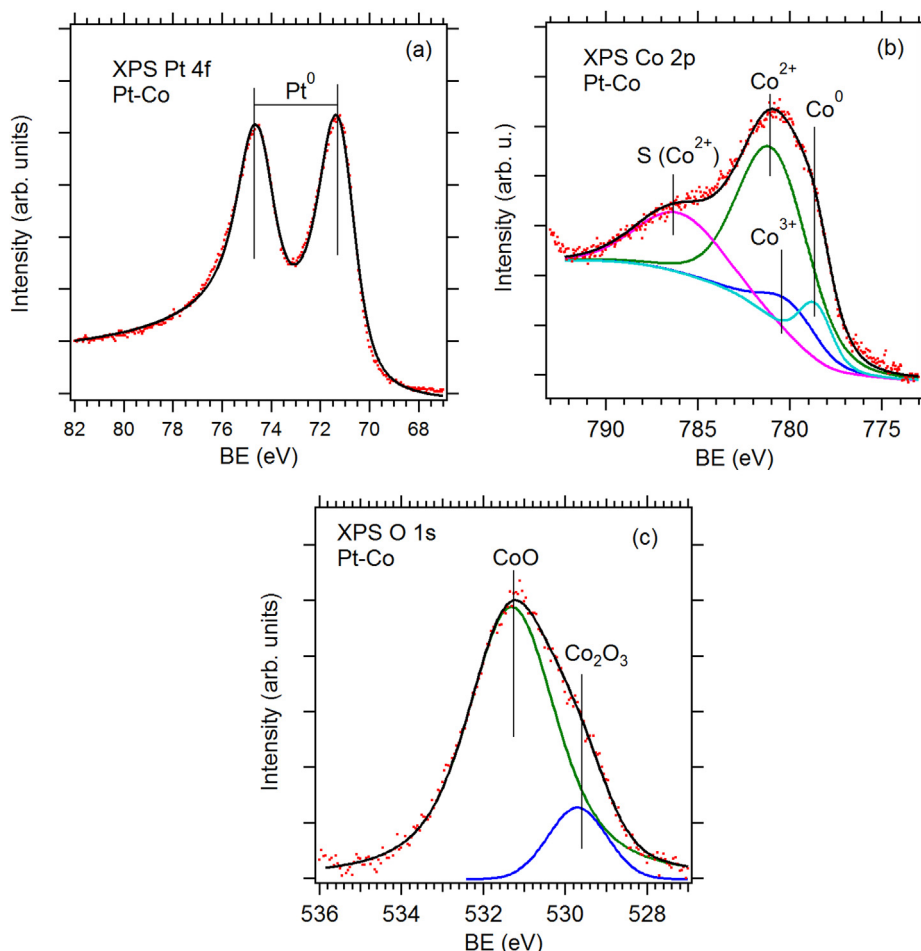


**Fig. 4.** Pt 4f XPS spectrum of the Pt–CeO<sub>x</sub> catalyst deposited on the nGDL after the humidified hydrogen annealing in the flow reactor.

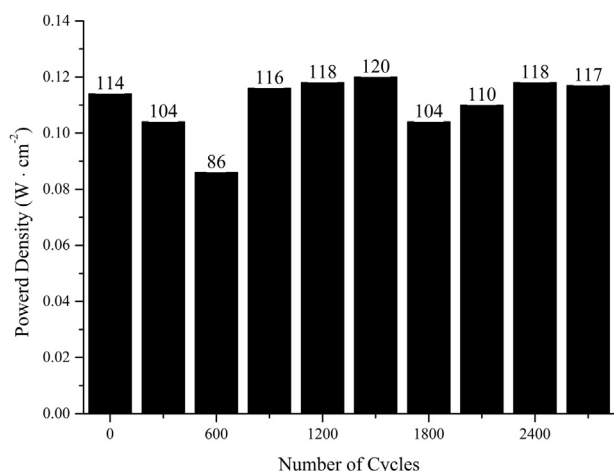
780.9 eV is a Co<sup>2+</sup> main peak whilst 786 eV peak corresponds to the satellite structure characteristic of octahedral Co<sup>2+</sup> cations [19]. The O 1s spectrum in Fig. 5(c) shows two peaks at 529.6 eV and 531 eV that could be assigned to Co<sub>2</sub>O<sub>3</sub> and CoO, respectively [20]. It is

evident that amount of cobalt oxides in the Pt–Co catalyst is substantially higher in relation to the metal Co content. The presence of high amount of oxidized Co in the Pt–Co catalyst could be explained by its exposure to air due to the sample transfer to the XPS spectrometer through air. We note that it is difficult to assign any of the mentioned XPS peaks to eventual Pt–Co alloy formation because Pt–Co alloy binding energy shifts for Pt 4f<sub>7/2</sub> and Co 2p<sub>3/2</sub> in relation to pure metals are very small, 0.1 eV and 0.2 eV, respectively [21].

The MEA durability test of the presented PEMFC was performed by using load cycling, i.e. using conditions in which the catalysts generally lose their activity rapidly. During the test 2700 loads giving current density of 1 A cm<sup>−2</sup> were applied during 30 s and followed by 30 s of open circuit state generating open circuit voltage (OCV). Generally due to sudden and dramatic load increase the anode experiences short periods of fuel starvation causing it to decay faster than at a constant load mode. The Pt oxidation state changes between reduced and oxidized form which also might accelerate damage of the anode. Setting at OCV also accelerates decay of the cell due to higher cathode voltage and reactant crossover rate [22]. During the test OCV was measured continuously and I–V FC characteristics were measured after each 300 cycles. The endurance test results are shown in Fig. 2 where we compared I–V FC characteristics obtained immediately before the endurance test with that obtained after 2700 cycles. Fig. 6 shows that our PEMFC performance exhibited some variations of maximum PD vs. number of cycles; however average value of PD exhibited only small decrease of performance.



**Fig. 5.** XPS Pt 4f (a), Co 2p<sub>3/2</sub> (b) and O 1s (c) spectra of the Pt–Co catalyst deposited on the nGDL.



**Fig. 6.** The dependence of MEA performance of the presented fully TF PEMFC on the number of the endurance test cycles.

#### 4. Conclusion

By summarizing the above presented results we can conclude that thin film technology, particularly magnetron sputtering, can be successfully used for fabrication of PEMFCs. Moreover it is shown that co-sputtering and depositing of mixed oxide and bimetallic systems are opening significantly easier way of state-of-the-art fuel cell catalyst preparation relative to standard wet techniques. Significant advantage of thin film catalyst use is in very good control of deposition parameters and film thickness permitting to prepare electrodes with very small and well controllable catalyst loading. Moreover sputtering technology permits to catalyze the support, e.g. GDL, in short time of few minutes without necessity to use another chemical process.

FC tests revealed high durability at power density of 125 mW cm<sup>-2</sup> with 50 µg of Pt per 1 cm<sup>2</sup> of membrane electrode assembly (MEA) (2 µg and 48 µg Pt cm<sup>-2</sup> for anode and cathode, respectively) giving Pt mass activity of 2.5 kW g<sup>-1</sup>. The endurance test presented above shows that the thin film catalysts might be very stable and do not reveal sintering or other morphological changes.

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#### References

- [1] K. Jukk, J. Kozlova, P. Ritslaid, V. Sammelselg, N. Alexeyeva, K. Tammeveski, *J. Electroanal. Chem.* 708 (2013) 31–38.
- [2] D. Fofana, S.K. Natarajan, J. Hamelin, P. Benard, *Energy* 64 (2014) 398–403.
- [3] I. Radev, G. Topalov, E. Lefterova, G. Ganske, U. Schnakenberg, G. Tsoitridis, E. Slavcheva, *Int. J. Hydrogen Energy* 37 (2012) 7730–7735.
- [4] G. Topalov, G. Ganske, E. Lefterova, U. Schnakenberg, E. Slavcheva, *Int. J. Hydrogen Energy* 36 (2011) 15437–15445.
- [5] V. Matolin, I. Matolinova, M. Vaclavu, I. Khalakhan, M. Vorokhta, R. Fiala, I. Pis, Z. Sofer, J. Poltierova-Vejpravova, T. Mori, V. Potin, H. Yoshikawa, S. Ueda, K. Kobayashi, *Langmuir* 26 (2010) 12824–12831.
- [6] V. Matolin, M. Cabala, I. Matolinova, M. Skoda, M. Vaclavu, K.C. Prince, T. Skala, T. Mori, H. Yoshikawa, Y. Yamashita, S. Ueda, K. Kobayashi, *Fuel Cells* 10 (2010) 139–144.
- [7] R. Fiala, I. Khalakhan, I. Matolinova, M. Vaclavu, M. Vorokhta, Z. Sofer, S. Huber, V. Potin, V. Matolin, *J. Nanosci. Nanotechnol.* 11 (2011) 5062–5067.
- [8] A. Bruix, Y. Lykhach, I. Matolinova, A. Neitzel, T. Skala, N. Tsud, M. Vorokhta, V. Stetsovych, K. Sevcikova, J. Myslivecek, R. Fiala, M. Vaclavu, K.C. Prince, S. Bruyere, V. Potin-Heurtaux, F. Illas, V. Matolin, K.M. Neyman, J. Libuda, *Angew. Chem. Int. Ed.* (2014), <http://dx.doi.org/10.1002/anie.201402342>.
- [9] V. Matolin, US Patent 8435921, 2013.
- [10] A. Stassi, I. Gatto, G. Monforte, V. Baglio, E. Passalacqua, V. Antonucci, A.S. Arico, *J. Power Sources* 208 (2012) 35–45.
- [11] M.V. Lebedeva, V. Pierron-Bohnes, C. Goyhenex, V. Papaefthimiou, S. Zafeirotas, R.R. Nazmutdinov, V. Da Costa, M. Acosta, L. Zosiak, R. Kozubski, D. Muller, E.R. Savinova, *Electrochim. Acta* 108 (2013) 605–616.
- [12] P. Hernandez-Fernandez, S. Rojas, P. Ocon, J.L.G. de la Fuente, P. Terreros, M.A. Pena, J.L. Garcia-Fierro, *Appl. Catal. B Environ.* 77 (2007) 19–28.
- [13] P. Hirunsit, P.B. Balbuena, *Surf. Sci.* 603 (2009) 912–920.
- [14] [http://www1.eere.energy.gov/office\\_eere/pdfs/budget/fuelcells\\_ataglance\\_2014.pdf](http://www1.eere.energy.gov/office_eere/pdfs/budget/fuelcells_ataglance_2014.pdf).
- [15] I. Khalakhan, M. Dubau, S. Haviar, J. Lavkova, I. Matolinova, V. Potin, M. Vorokhta, V. Matolin, *Ceram. Int.* 39 (2013) 3765–3769.
- [16] B. Patrick, H.C. Ham, Y. Shao-Horn, L.F. Allard, G.S. Hwang, P.J. Ferreira, *Chem. Mater.* 25 (2013) 530–535.
- [17] M. Schoemaker, U. Misz, P. Beckhaus, A. Heinzel, *Fuel Cells* 14 (2014) 412–415.
- [18] C.D. Wagner, W.M. Riggs, L.E. Davies, J.F. Moulder, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin Elmer Corporation, 1978.
- [19] S.C. Petitto, E.M. Marsh, G.A. Carson, M.A. Langell, *J. Mol. Catal. A Chem.* 281 (2008) 49–58.
- [20] T.J. Chuang, C.R. Brundle, D.W. Rice, *Surf. Sci.* 59 (1976) 413–429.
- [21] Y.S. Lee, J.Y. Rhee, C.N. Whang, Y.P. Lee, *Phys. Rev. B* 68 (2003) 235111–1–235111-7.
- [22] Z. Qi, *Proton Exchange Membrane Fuel Cell*, CRC Press, Boca Raton, 2014.